

The Half-Metallicity of Zigzag Graphene Nanoribbons with Asymmetric Edge Terminations

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The spin-polarized electronic structure and half-metallicity of zigzag graphene nanoribbons (ZGNRs) with asymmetric edge terminations are investigated by using first principles calculations. It is found that compared with symmetric hydrogen-terminated counterparts, such ZGNRs maintain a spin-polarized ground state with the anti-ferromagnetic configuration at opposite edges, but their energy bands are no longer spin degenerate. In particular, the energy gap of one spin orientation decreases remarkably. Consequently, the ground state of such ZGNRs is very close to half-metallic state, and thus a smaller critical electric field is required for the systems to achieve the half-metallic state. Moreover, two kinds of studied ZGNRs present massless Dirac-fermion band structure when they behave like half-metals.

Keywords: Graphene Nanoribbon, Edge Termination, Half-Metallicity, Energy Gap, Electric Field

1. INTRODUCTION

Due to recent progress in preparing single graphite layer,¹⁻⁵ graphene, this two-dimension (2D) electronic system has attracted extensive interest. Importantly, graphene can be patterned via standard lithographic technique into new carbon based quasi-one-dimension materials,^{6,7} graphene nanoribbons (GNRs), which have many properties similar to Carbon nanotubes (CNTs), such as energy gap dependence of widths and crystallographic orientations,⁷⁻⁹ electronic confinement and long phase coherence length.⁶ Furthermore, different from CNTs, the planar geometry of GNRs allows for the more straightforward fabrication and better control of crystallographic orientation. All of these characteristics of GNRs provide an exciting possibility for the flexible design of GNR-based electronic devices in nanometer scale.^{10,11}

As one kind of GNRs, zigzag graphene nanoribbons (ZGNRs) have many peculiar and interesting properties because of the presence of the zigzag edges.^{9,12-23} On the one hand, ZGNRs have localized edge states¹²⁻¹⁵ and exhibit a spin-polarized semiconducting ground state,^{9,16-18} which is characterized by the anti-ferromagnetic (AF) configuration with opposite spin orientations between ferromagnetically ordered edge states at each edge. Particularly, although the energy bands of the ground state are spin degenerate, under an appropriate in-plane electric field perpendicular to the direction of the ribbon edge, ZGNRs are forced into a half-metallic state where one spin exhibits a metallic behavior, while the other experiences an increase in the bandgap.¹⁸⁻²¹ So ZGNRs could serve as spin filter devices in future nanospintronics. On the other hand, the edges of ZGNRs have unique chemical reactivity,²³ and

might be terminated by many chemical groups such as hydroxyl, carboxyl and epoxide groups.²⁴⁻²⁷ Moreover, it is predicted that edge oxidation could enhance the half-metallicity of ZGNRs,²⁸ and that asymmetric terminations could significantly change the electronic, magnetic and transport properties of ZGNRs.^{17,29-32} Therefore, the zigzag edges and edge termination groups (including their symmetries) play a significant role in the properties of ZGNRs, and it is essential to gain better understanding of the effect of asymmetric chemical edge terminations on the electronic properties of ZGNRs, especially the half-metallicity.

In this work, we investigate the relative stabilities, electronic structure and half-metallic nature of ZGNRs with asymmetric edge terminations, and the termination groups being considered include Hydrogen (H), hydroxyl (OH) and carboxyl (COOH). It is found that OH and COOH terminations are as stable as H termination. Compared with symmetric H-terminated ZGNRs which have been studied extensively,^{9,12,13,17,18} the ZGNRs we focus on maintain a spin-polarized ground state with the anti-ferromagnetic configuration, but their energy bands are no longer spin degenerate. Particularly, the energy gap for one spin orientation reduces remarkably, which leads to the fact that the ground state is very close to the half-metallic state. We show that such feature arises from the difference of electrostatic potentials at two edges induced by asymmetric edge terminations, so a smaller critical electric field compared with fully H-terminated ZGNRs is required to force the system into half-metallic state. These properties indicate that the half-metallicity of ZGNRs can be enhanced by breaking the symmetry of edge terminations via chemical treatments, and offer a possibility for the design of spin filter devices based on asymmetric terminated ZGNRs.

2. CALCULATION METHOD AND MODEL

Our electronic structure calculations were performed using the SIESTA method,³³ which is based on the *ab*

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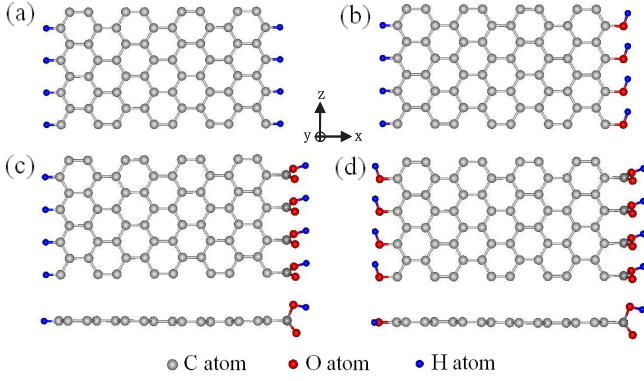


FIG. 1: Optimized geometry of zigzag graphene nanoribbons with different edge terminations. (a) 8-ZGNR-H-H. (b) 8-ZGNR-H-OH. (c) 8-ZGNR-H-COOH. (d) 8-ZGNR-OH-COOH. In (c) and (d), both top and side views are shown. The gray, red, and blue balls represent Carbon, Oxygen, and Hydrogen atoms respectively. The z axis is taken along the periodic direction of ZGNRs, and the x axis is along the direction of external electric field.

initio density-functional theory (DFT) within the local spin density approximation (LSDA).³⁴ The structure optimizations were first carried out until atomic forces converged to 0.02 eV/Å, and the mesh cutoff energy is chosen as 200 Ry. To simulate an isolated graphene nanoribbon, we adopted a three-dimensional repeating model in which each nanoribbon is separated by 8 Å for both edge-edge and layer-layer intervals, and the supercell length a along z (periodic) direction of ZGNRs (Fig. 1) is set to be 2.461 Å. Moreover, a periodic saw-tooth-type potential along x direction is used to simulate the external in-plane electric fields in a supercell.

In accordance with previous convention,^{9,12,13,16–18} the ZGNRs are classified by the number of zigzag C-C chains forming the width of the ribbon, and the ZGNR with n zigzag C-C chains is named as n -ZGNR. Herein symmetric H-terminated ZGNRs are named as ZGNRs-H-H (as shown in Fig. 1(a)), and three kinds of ZGNRs with asymmetric edge terminations are mainly considered in our study:

- (1) the left and right edges are respectively terminated by H and hydroxyl group (ZGNRs-H-OH), as shown in Figure 1(b);
- (2) the left and right edges are respectively terminated by H and carboxyl group (ZGNRs-H-COOH), as shown in Figure 1(c);
- (3) the left and right edges are respectively terminated by hydroxyl and carboxyl groups (ZGNRs-OH-COOH), as shown in Figure 1(d).

3. RESULTS AND DISCUSSION

We start by studying the relative stability of the ground states of ZGNRs terminated by different functional groups. First, for the ZGNRs terminated by OH or COOH groups, the localized edge states still exist be-

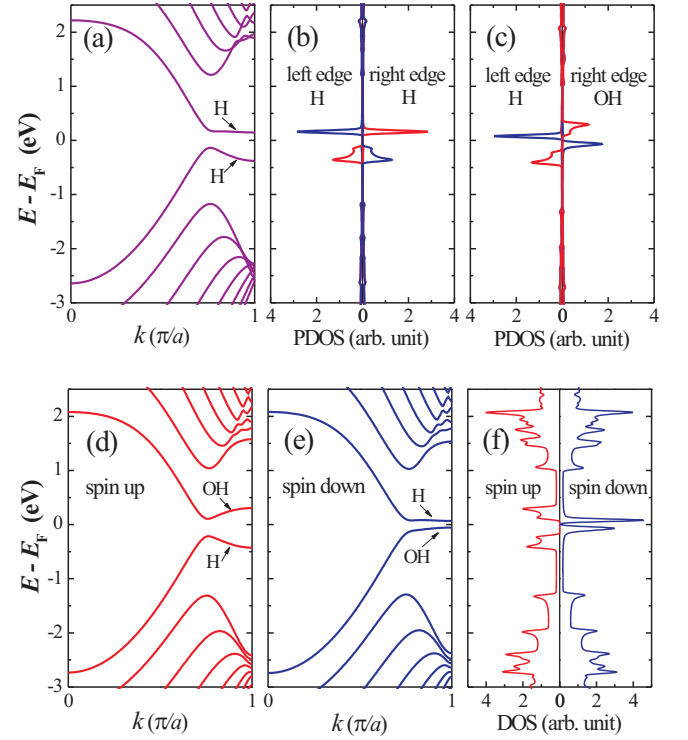


FIG. 2: (a) The spin-degenerate energy band structure of 8-ZGNR-H-H in AF configuration. (b), (c) PDOS of two edge carbon atoms in 8-ZGNR-H-H and 8-ZGNR-H-OH respectively, where red (blue) lines are associated with spin up (down). (d) Spin-up and (e) spin-down energy bands, and (f) the total DOS of 8-ZGNR-H-OH in AF configuration. In (a), (d) and (e), the arrows indicate the edge states and which edge they are localized at.

cause of the maintenance of sp^2 hybridization of edge carbon atoms, and their ground states are also spin-polarized and in anti-ferromagnetic configuration like fully H-terminated ZGNRs. In addition, our calculations show that the binding energies³⁵ of a 8-ZGNR-H (one edge is terminated by H, while the other is bare) and three kinds of functional groups (H, OH and COOH) are -5.7, -6.3, and -5.5 eV, respectively. These results indicate that OH and COOH terminations do not change the spin configuration of the ground state of ZGNRs, and they are as stable as H termination.

Now the electronic properties of the ZGNRs are studied, and asymmetric edge terminations are shown in Figure 1. As revealed in the previous study,¹⁸ an important feature of the ground states of ZGNRs-H-H is that their energy bands are spin degenerate (shown in Fig. 2(a)). However, it is found that such feature does not exist in the studied ZGNRs with asymmetric edge terminations, and their energy gaps for one spin orientation reduce remarkably. In the following, 8-ZGNRs are chosen as examples for detailed discussions, because ZGNRs with different width exhibit similar basic characteristics of electronic structure.

A typical band structure and density of states (DOS)

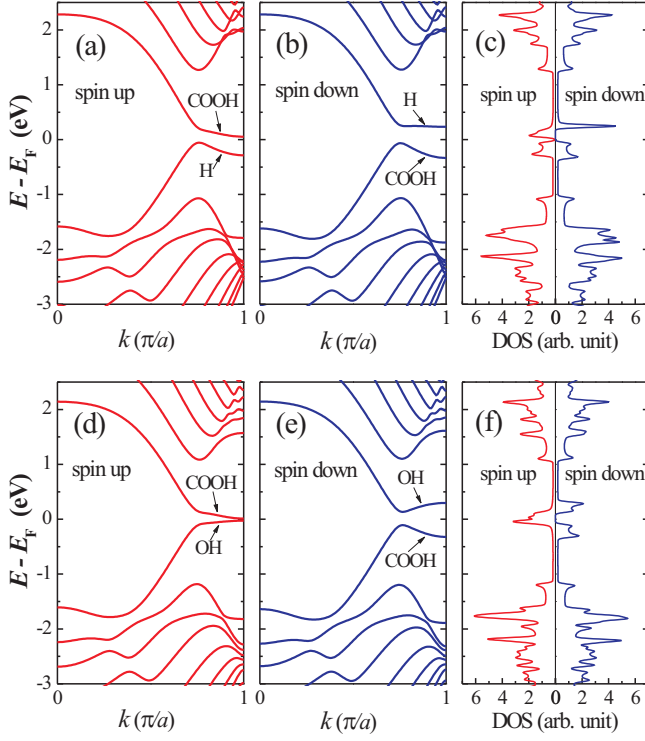


FIG. 3: (a) Spin-up and (b) spin-down energy bands, and (c) the total DOS of 8-ZGNR-H-COOH in AF configuration. (d) Spin-up and (e) spin-down energy bands, and (f) the total DOS of 8-ZGNR-OH-COOH in AF configuration. In (a), (b), (d) and (e), the arrows indicate the edge states and which edge they are localized at.

for 8-ZGNR-H-OH are shown in Figures 2(d, e and f). Compared with 8-ZGNR-H-H, energy bands for opposite spin are no longer degenerate, and the energy gap of spin-up bands (0.32 eV) is larger than that of spin-down bands (0.12 eV). It is found that this spin splitting arises from the influence of asymmetric edge terminations on the electrostatic potentials of edge carbon atoms. For 8-ZGNR-H-H, projected DOS (PDOS) of edge carbon atoms (Fig. 2(b)) indicates that the energies of edge states localized at left and right edges are the same due to the equal electrostatic potentials at two edges, so the energy gaps associated with spin-up and spin-down are equal. Whereas for 8-ZGNR-H-OH, because of the difference of electrostatic potentials at two edges caused by asymmetric edge terminations, the energies of edge states localized at left (H-terminated) edge are lower than that of states localized at right (OH-terminated) edge, as PDOS of edge carbon atoms (Fig. 2(c)) illustrated. In addition, the states localized at two edges for each spin are occupied and unoccupied states respectively, so the energy difference of left and right edge states leads to the unique behavior that the energy gap associated with one spin increases, whereas that associated with the other decreases (as shown in Fig. 2(c)).

Like 8-ZGNR-H-OH, the energy bands of 8-ZGNR-H-COOH in the anti-ferromagnetic configuration (shown in

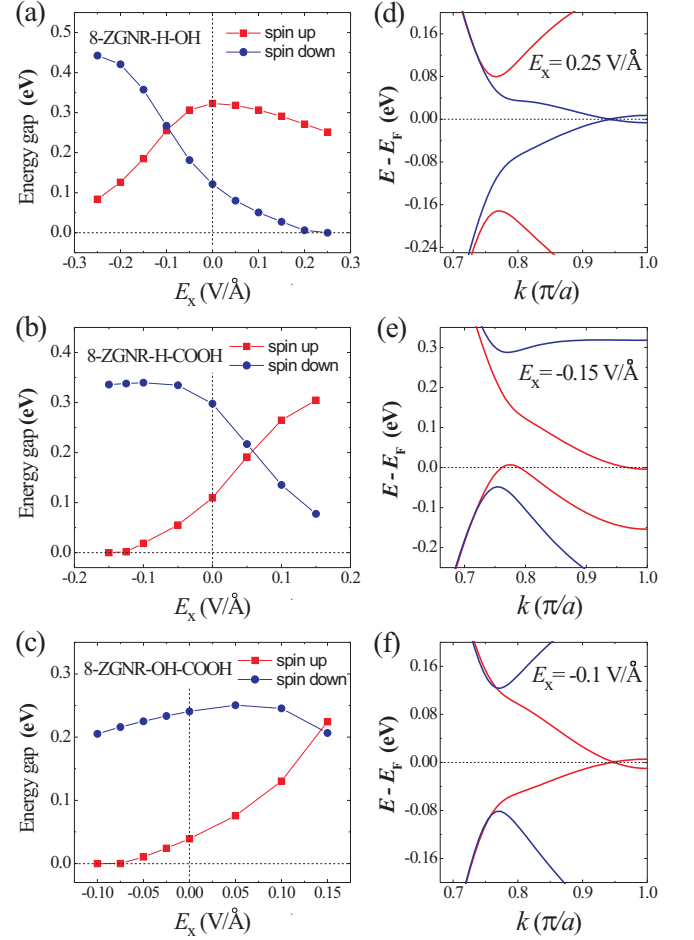


FIG. 4: Electric field effect on the spin-polarized bandgaps of (a) 8-ZGNR-H-OH, (b) 8-ZGNR-H-COOH, and (c) 8-ZGNR-OH-COOH, where positive E_x represents that the direction of electric fields is from left edge to right edge of ZGNRs, while negative E_x represents the opposite direction. (d), (e), (f) The spin-resolved band structures corresponding to (a), (b), and (c) when the systems achieve the half-metallic states, where red (blue) lines represent spin up (down).

Figs. 3(a and b)) are also spin split around the Fermi level because of the asymmetry of edge terminations. In contrast to 8-ZGNR-H-OH, however, the relative small energy gap (0.11 eV) appears in the spin-up bands rather than in the spin-down bands, and the energies of states localized at H-terminated edge are higher than that of states localized at COOH-terminated edge. This difference indicates that the changes of the electrostatic potential of edge carbon atoms induced by OH and COOH are opposite, and implies that 8-ZGNR-OH-COOH would have a larger difference between electrostatic potentials at two edges and a smaller energy gap for one spin orientation. Our further calculations confirm this viewpoint and show that the energy gap associated with spin-down is 0.24 eV, and that associated with spin-up is only 0.04 eV (Figs. 3(d) and 3(e)). Therefore, the ground state of 8-ZGNR-OH-COOH is very close to half-metallic state.

As mentioned above, the ZGNRs considered in our study maintain the edge states and anti-ferromagnetic configuration like ZGNRs-H-H. Therefore, one would expect that these systems behave as half-metals under the influence of an appropriate external electric field. To substantiate this presumption, we have calculated the energy gaps of spin-up and spin-down bands as a function of the intensity of an external electric field along the x direction (E_x), which are shown in Figure 4, where positive E_x represents that the direction of electric fields is from left edge to right edge of ZGNRs, while negative E_x represents the opposite direction.

For 8-ZGNR-H-OH, Figure 4(a) shows that the energy gap of spin-down bands decreases successively as E_x increases, and becomes zero when E_x reaches 0.21 V/Å. At the same time, the energy gap of spin-up bands remains very large, which means that the system has become half-metallic. Similar to 8-ZGNR-H-OH, 8-ZGNR-H-COOH and 8-ZGNR-OH-COOH also exhibit half-metallic behaviors under the influence of an external electric field, as shown in Figures 4(b and c). However, it is noticeable that for 8-ZGNR-H-COOH and 8-ZGNR-OH-COOH, the E_x that make the systems achieve half-metallic states is negative rather than positive like 8-ZGNR-H-OH, because the energies of left edge states are lower than that of right edge states in 8-ZGNR-H-OH (Fig. 2(c)), whereas the situation is opposite in 8-ZGNR-H-COOH and 8-ZGNR-OH-COOH. Thus, the directions of electric fields that can efficiently force the systems into half-metallic states are different for these ZGNRs.

It is interesting to note that the absolute values of critical electric fields required to achieve half-metallic states for the later two kinds of ZGNRs are 0.13 and 0.07 V/Å respectively, which are much smaller than that of 8-ZGNR-H-H (this value given by our calculations is 0.22 V/Å). Such characteristic results from the fact that the energy gap for one spin orientation has already reduced without external electric fields. Therefore, the half-metallic states can be achieved more easily due to

asymmetric edge terminations, and such ZGNRs could serve as the spin filter devices even without the application of an external electric field. Figures 4(d, e and f) show the spin-resolved band structures of three studied ZGNRs in the half-metallic state. It is found that for ZGNRs-H-OH and ZGNRs-OH-COOH, only two bands for one spin orientation cross at the Fermi level, which indicates that their charge carriers mimic massless Dirac fermions similar to the experimental observation in graphene.⁴ However, this property does not exist in ZGNRs-H-H¹⁸ and ZGNRs-H-COOH (Fig. 4(e)) since they have indirect energy gaps before they are forced into half-metallic states.

4. CONCLUSION

In conclusion, the influence of asymmetric edge terminations on the spin-polarized electronic structure of ZGNRs is studied using *ab initio* calculations. It is found that different edge termination groups can change the energies of edge states of ZGNRs without breaking the original spin-polarized anti-ferromagnetic configuration, thus asymmetric edge terminations can lead to a spin splitting of energy bands around the Fermi level. Most importantly, the energy gap of one spin orientation almost disappears, which means the ground state is very close to the half-metallic state. Thus, changing edge termination groups via chemical treatments is an effective way to reduce the required critical electric field to make ZGNRs achieve half-metallic states, and even can make their ground states half-metallic directly. This effect provides a promising possibility of using ZGNRs as spin filter devices in future nanospintronics.

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